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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] this invention relates to the nickel and the hydrogen battery using the nickel positive electrode for alkaline batteries and this which come to support the active material which makes a nickel oxide a principal component by the conductive core material still in detail about the nickel and the hydrogen battery which used the nickel positive electrode for alkaline batteries, and this.

[0002]

[Description of the Prior Art] As a rechargeable battery, the nickel cadmium battery (a nickel-cadmium battery is called hereafter) which are a lead accumulator and an alkaline battery is used broadly now. Although a lead accumulator is cheap, generally the energy density per unit weight (Wh/kg) is low, there is a technical problem in a cycle life etc., and it cannot be said that it is suitable as a power supply of a small lightweight portable device. On the other hand, compared with a lead accumulator, a unit weight and the energy density of a nickel-cadmium battery per volume are high, and since it excels in reliability, such as a cycle life, it is broadly used as a power supply for each portable devices.

[0003] However, since the load to a cell is increasing with value[with quantity]-izing of a portable device in recent years, it is further anxious for the rechargeable battery of high-energy density as a power supply for portable devices.

[0004] then, in the field of a nickel-cadmium battery, high capacity-ization which is a nickel-cadmium battery using the conventional sintering formula nickel positive electrode progresses, and the nickel-cadmium battery using the foaming metal formula nickel positive electrode which is 30 - 60% high capacity is also developed from this. Furthermore, the nickel and the hydrogen battery which used the hydrogen storing metal alloy for the negative electrode which is high capacity rather than the nickel-cadmium battery again are developed. This nickel and hydrogen battery have the capacity more than the double precision of the nickel-cadmium battery which used the sintering formula nickel positive electrode.

[0005] In order that these high capacity alkaline batteries may raise the energy density of a positive electrode, what filled up with nickel hydroxide powder the latter nickel porous body of foaming and nickel fiber porous body of a sintering formula nickel porous body and the three dimensions which have 90% or more of porosity with high density as a positive electrode is used. Consequently, to the energy density of the conventional sintering formula nickel positive electrode being 400 - 450 mAh/cm³, it of the latest

sintering formula nickel positive electrode improved to 450 - 500 mAh/cm³, and it of the letter nickel positive electrode of foaming improved to 550-650.

[0006] however, a sintering formula nickel porous body, the letter nickel porous body of foaming, and nickel fiber porosity -- although the energy density near ordinary temperature of the positive electrode which filled up the inside of the body with nickel hydroxide with high density is high, there is a problem that an energy density falls under elevated-temperature atmosphere. Therefore, it is difficult to harness the feature of high-energy density by the broad temperature requirement.

[0007] This cause is for an oxygen-evolution reaction to become easy to occur simultaneously with the charge reaction to nickel hydroxide in the charge under elevated-temperature atmosphere. That is, it is for the oxygen-evolution overvoltage in a positive electrode to decrease, and for nickel hydroxide not to be enough charged by oxy-nickel hydroxide, but for the utilization factor of nickel hydroxide to fall.

[0008] In order to solve this problem, in JP,61-104565,A, the method of adding cadmium-oxide powder and cadmium-hydroxide powder all over a positive electrode and the method of making a cadmium oxide contain inside nickel hydroxide powder are proposed. According to these proposals, the utilization factor of the nickel hydroxide under elevated-temperature atmosphere can be raised, and the fall of the energy density under elevated-temperature atmosphere can be suppressed to some extent.

[0009]

[Problem(s) to be Solved by the Invention] However, in the grade of the addition of the cadmium oxide in the above-mentioned proposal, the utilization factor of the nickel hydroxide under elevated-temperature atmosphere is about 80%, and in order to raise it further, it needs to increase the addition of the cadmium oxide to the inside of the interior of nickel hydroxide, or a nickel positive electrode. Thus, although the utilization factor of the nickel hydroxide under elevated-temperature atmosphere can be raised to about 90% by increasing the addition of a cadmium oxide, there is a problem that the utilization factor of the nickel hydroxide near ordinary temperature falls to about 80% conversely.

[0010] Moreover, the nickel and the hydrogen battery which does not contain the cadmium which is heavy metal from a viewpoint of an environmental problem attract attention in recent years. However, when cadmium and cadmium powder are removed out of nickel hydroxide or a positive electrode, there is a problem that the utilization factor of the nickel hydroxide under elevated-temperature atmosphere will fall to about 50 - 60% with a natural thing.

[0011] this invention aims at offering the nickel and the hydrogen battery which was excellent in service capacity under a broad temperature atmosphere, without containing heavy metal, such as a nickel positive electrode for alkaline batteries which was excellent in the utilization factor of nickel hydroxide under a broad temperature atmosphere, and cadmium, by easy composition.

[0012]

[Means for Solving the Problem] The nickel positive electrode for alkaline batteries by this invention is characterized by adding a kind at least among the compounds of an yttrium, an indium, antimony, barium, calcium, and beryllium to an active material in the nickel positive electrode which comes to support the active material which makes a nickel oxide a principal component by the conductive core material.

[0013] the above -- an yttrium -- an indium -- antimony -- barium -- calcium -- and --

beryllium -- a compound -- ***** -- Y -- two -- O -- three -- Y -- (-- OH --) -- three -- In -- two -- O -- three -- In -- two -- O -- In -- two -- O -- three -- -- H -- two -- O -- Sb -- two -- O -- three -- Sb -- two -- O -- four -- Ba -- (-- OH --) -- two -- CaO

[0014] As for the addition of the compound of the above-mentioned yttrium, an indium, antimony, barium, calcium, and beryllium, it is desirable to consider as 0.1 - 5 weight section to the nickel-oxide 100 weight section.

[0015] Moreover, to the above-mentioned active material, the thing of cobalt and a cobalt oxide for which a kind is further added at least among a kind and/or the cadmium oxide, and the zincic-acid ghost is desirable.

[0016] In this case, the above-mentioned cobalt oxide is cobalt hydroxide, a zincic-acid ghost is a zinc oxide, nickel hydroxide:cobalt:cobalt hydroxide:zinc-oxide:(inside of compound of yttrium, indium, antimony, barium, calcium, and beryllium at least kind) =100:4-18:0-10:0-10:0.1-5 come out comparatively, and a certain thing is desirable at a weight ratio.

[0017] As for the above-mentioned conductive core material, it is desirable that they are the letter nickel porous body of foaming, a sintering formula nickel porous body, and one three-dimensions porous body of the punching metals.

[0018] Or the above-mentioned conductive core material is monotonous, and it is desirable to perform nickel plating to a nickel foil or an iron foil.

[0019] As for the above-mentioned letter nickel porous body of foaming, it is desirable for the surface density to be 200 - 700 g/m².

[0020] It is desirable for the above-mentioned nickel oxide to be the nickel hydroxide which contained a kind 1 to 7% as the solid solution inside the crystal at least among spherical nickel hydroxide or cadmium, zinc, lead, silver, an indium, an yttrium, magnesium, iron, cobalt, and manganese.

[0021] When the above-mentioned nickel oxide is spherical nickel hydroxide, the mean particle diameter is 7-20 micrometers, and, as for the above-mentioned nickel hydroxide powder, it is desirable for the tap density to be the spherical particle of three or more [1.9g //cm]. Moreover, it is desirable to set the BET specific surface area measured by adsorption of nitrogen gas in this case as 10-30m³/g.

[0022] As for the above-mentioned active material, it is desirable to contain the powder which has waterproofed characteristics. Furthermore, the nickel positive electrode where the nickel and the hydrogen battery of this invention come to support the active material which makes a nickel oxide a principal component by the conductive core material, In nickel and a hydrogen battery equipped with the negative electrode which makes a subject electrochemically the hydrogen storing metal alloy in which the occlusion release reaction of hydrogen is possible, the alkali electrolytic solution, separator, the case where these are held, and the obturation board that has a relief valve It is characterized by adding a kind at least among the compounds of an yttrium, an indium, antimony, barium, calcium, and beryllium to the aforementioned active material.

[0023] As for the alkali electrolytic solution, in the above-mentioned nickel and hydrogen battery, it is desirable that it is the thing of a potassium hydroxide and a sodium hydroxide which consists of a kind and a lithium hydroxide at least. Moreover, as for a lithium hydroxide, it is desirable to contain 10 or more g/l in the electrolytic solution. Furthermore, it is desirable for zincic-acid ion to exist in the alkali electrolytic solution.

[0024] It is good to use as separator the nonwoven fabric which performed sulfone

processing. As for the valve working pressure of a relief valve, it is desirable to make it set as 5 - 30 kg/cm³.

[0025]

[Function] The above composition, i.e., by adding a kind at least among the compounds of an yttrium, an indium, antimony, barium, calcium, and beryllium in the active material of a nickel positive electrode, these compounds stick to the front face of the nickel oxide which is an active material, and the overvoltage which is the competitive reaction in the charge under elevated-temperature atmosphere is increased. Consequently, the charge reaction to the oxy-nickel hydroxide of the nickel hydroxide which is a nickel oxide is fully performed, and the utilization factor under elevated-temperature atmosphere improves. Moreover, unlike a cadmium oxide, these compounds do not affect the utilization factor of the nickel oxide in the atmosphere below ordinary temperature. Therefore, the positive electrode which was excellent in the broad temperature requirement at the active material utilization factor was obtained by making a positive active material contain a compound. Moreover, in the nickel and the hydrogen battery from which cadmium was removed, the nickel and the hydrogen battery which has the electric discharge property which was excellent in a broad temperature atmosphere were obtained by using the positive electrode containing the above-mentioned compound.

[0026]

[Example] Hereafter, the nickel and the hydrogen battery using the nickel positive electrode for alkaline batteries and it by the desirable example of this invention are explained, referring to an accompanying drawing.

an example 1 -- the positive electrode was created as follows first

[0027] As a nickel oxide which is a positive active material, cobalt and cadmium prepared for the interior the spherical nickel hydroxide powder contained as 0.3wt(s)% and the 3.0wt% solid solution, respectively. Cobalt hydroxide was used as oxide cobalt powder, using carbonyl cobalt as cobalt powder.

[0028] Y₂O₃ as these powder, cadmium-oxide powder, and additive powder, In₂O₃, Sb₂O₃, and calcium(OH)₂ were mixed so that it might become the composition and the mixing ratio (weight ratio) of A-J which were shown in Table 1. In this way, after having added water to the made mixture, mixing and making it the shape of a paste, it was filled up to the letter nickel porous body of foaming of 95% of porosity, and surface density 300 g/m² which is a base material, and in order to prevent defluxion of the powder from a plate front face, it was immersed in the solution which fluororesin powder distributed after dryness and pressurization. Then, the nickel positive electrode of sample A-J shown for cutting in a predetermined size after dryness again (Table 1) was created. Sample A-F is the example of this invention, and sample G-J is an example of comparison.

[0029]

[Table 1]

各正極板の組成と混合比

No.	Ni(OH) ₂	Co	Co(OH) ₂	CdO	添加物
A	1 0 0	7	5	3	3 (Y ₂ O ₃)
B	1 0 0	7	5	3	3 (In ₂ O ₃)
C	1 0 0	7	5	3	3 (Sb ₂ O ₃)
D	1 0 0	7	5	3	3 (Ba(OH) ₂)
E	1 0 0	7	5	3	3 (Ca(OH) ₂)
F	1 0 0	7	5	3	3 (Ba OH) ₂)
G	1 0 0	7	5	0	0
H	1 0 0	7	5	3	0
I	1 0 0	7	5	5	0
J	1 0 0	7	5	7	0

[0030] Next, these positive electrodes were made into the operation pole, the half cell was constituted, using a nickel network as a counter electrode, and the utilization factor of active material **** nickel hydroxide was examined. The mercury-oxide electrode was used for the reference electrode.

[0031] Under each atmosphere (0 degree C, 20 degrees C, and 45 degrees C), the active material utilization factor charged the operation pole with the current density of 0.1CmA

to 150% of positive-electrode capacity, i.e., the geometric capacity calculated from a nickel hydroxide active material, performed the pause for 3 hours, performed continuous discharge to 0.1V to the mercury-oxide electrode by the low-current density of 0.2CmA(s) under 20-degree-C atmosphere, and calculated it using the following formula. [0032] Active material utilization factor = (data A-F and the active material utilization factor of the positive electrode of each G-J were shown in the service capacity / nickel hydroxide geometric capacity x100 drawing 1 , and drawing 2 to 0.1V.) Although the utilization factor in 45 degrees C will improve from 56% to 88% if the addition of a cadmium oxide is increased to 7wt(s)% so that clearly also from the result of drawing 2 , the utilization factor in 20 degrees C will fall to about 80%. On the other hand, as shown in drawing 1 , in the positive electrode of composition of example A-F, it turns out that a utilization factor [in / 82 - 93% and 20 degrees C / in the utilization factor in 45 degrees C] shows the utilization factor which whose utilization factor in 0 degree C is 97 - 105%, and was excellent over the broad temperature requirement 95 to 100%. It is because the charge reaction to the oxy-nickel hydroxide of nickel hydroxide is fully performed that the compound added in example A-F raises the active material utilization factor under elevated-temperature atmosphere, in order for this compound to stick to the front face of the nickel oxide which is an active material and to raise the overvoltage of the oxygen evolution which is the competitive reaction of the charge under elevated-temperature atmosphere. The additive used by this example has the advantage which can raise the utilization factor in an elevated temperature, without reducing the utilization factor in ordinary temperature compared with a cadmium oxide.

[0033] In addition, it is desirable to consider as the range of 0.1 - 5 weight section in the example, although the addition of an additive was made into 3 weight sections to the nickel hydroxide 100 weight section. When it increases from 5 weight sections, it is for the amount of adsorption of the compound which is an additive to the front face of the nickel hydroxide which is an active material to increase, for the surface area of an active material effective in an electric discharge reaction to decrease, for discharge voltage to fall by this, and for an electric discharge property to deteriorate. Moreover, improvement in the utilization factor under elevated-temperature atmosphere is not accepted below in the 0.1 weight sections. Moreover, in this example, although the oxide and the hydroxide were mentioned as a compound to add, compounds, such as a sulfate and a chloride, may be used and the same effect is acquired.

[0034] In this example, although surface density used 300g/the letter nickel porous body of foaming of m2 for the base material, if surface density is the range of 200 - 700 g/m2, the same effect will be done so. Moreover, besides the letter nickel porous body of foaming, even if it uses the punching metal and plate which are a kind of a three-dimensions porous body, the same effect is acquired.

[0035] Although this example explained 0.3wt% for the amount of the cadmium which exists as the solid solution, and cobalt as an example 3.0wt(s)%, respectively, the same inclination is shown if it is the range of 1 - 7wt%. Moreover, the same effect is shown even if it uses zinc, lead, silver, an indium, an yttrium, iron, and manganese in addition to cadmium and cobalt.

Example 2 nickel and the hydrogen battery were created as follows.

[0036] First, the positive electrode was created as follows. First, the spherical nickel hydroxide powder with which the mean particle diameter contained zinc 3.5wt% and

cobalt 0.3wt% whose tap density a BET specific surface area is 22m²/g, and is 2.0 g/cm³ as the solid solution by 12 micrometers, cobalt powder, cobalt hydroxide powder, and each additive powder (a yttrium oxide --) Indium oxide, an antimony oxide, a barium hydroxide, a calcium hydroxide, Hydroxylation beryllium is mixed at a rate of 100:7:5:3 by the weight ratio. After adding and kneading water to this and making it the shape of a paste, it was filled up to the letter nickel porous body of foaming of 95% of porosity, and surface density 300 g/m² which is a base material, and in order to prevent defluxion of the powder from a plate front face, it was immersed in the solution which fluororesin powder distributed after dryness and pressurization. Then, it dried again and the nickel positive electrode which does not contain the cadmium which has the capacity of 1400mAh(s) which cut in the predetermined size and contained various additives was created after this dryness. Composition of a positive electrode was shown in (Table 2).

[0037]

[Table 2]

各正極板の組成と混合比

No.	Ni(OH) ₂	Co	Co(OH) ₂	添加物
K	100	7	5	3 (Y ₂ O ₃)
L	100	7	5	3 (In ₂ O ₃)
M	100	7	5	3 (Sb ₂ O ₃)
N	100	7	5	3 (Ba(OH) ₂)
O	100	7	5	3 (Ca(OH) ₂)
P	100	7	5	3 (Ba OH) ₂)
Q	100	7	5	0

[0038] The negative electrode was created as follows. In addition, alloy composition of a negative electrode was set to MmNi3.5, Co 0.7, Mn 0.4, and aluminum0.3 (Mm is the

mixture of rare earth elements at a misch metal).

[0039] First, after paying each ingredients of a misch metal Mn, and nickel, Co, Mn and aluminum which are the mixture of rare earth elements to an arc furnace and making it a vacua to 10^{-4} - 10^{-5} torr, arc discharge was carried out in the state of the reduced pressure under argon gas atmosphere, and the heating dissolution was carried out. In order to attain homogenization of a sample, ***** was performed at 1050 degrees C among the vacuum for 6 hours. The powder of 20 micrometers of mean particle diameters was obtained for the obtained alloy lump after coarse grinding using the wet ball mill. After processing stirring this powder in 80-degree C 7.2-mol potassium-hydroxide solution for 1 hour, the hydrogen storing metal alloy powder which rinses in order to remove a potassium hydroxide from the end of an alloy powder, and is used for a negative electrode by drying was obtained. Water and the carboxymethyl cellulose (CMC) were added to this hydrogen storing metal alloy, and it was made the shape of a paste, was filled up to the letter nickel porous body of foaming of 95% of porosity, and cut in the predetermined size after dryness and pressurization, and the hydrogen storing metal alloy negative electrode was created.

[0040] Separator circled in the negative electrode 1 and positive electrode 2 using the sulfonation separator which sulfonated the nonwoven fabric which consists of polypropylene and polyethylene for the purpose of the reduction in self-discharge which were created as mentioned above in the shape of a whorl through separator 3, as shown in drawing 3, and it inserted them in the case 4 which serves as a negative-electrode terminal. And the alkali electrolytic solution which carried out 40 g/l dissolution of the LiOH-H₂O was poured in three times 2.4cm into the potassium-hydroxide solution whose specific gravity is 1.30, finally the case 4 was obturated with the obturation board 7 equipped with the relief valve 6 which operates with ten to 20 atmospheric pressure, and the sealed type nickel and the hydrogen battery of six kinds of 4/5 sizes using the positive electrode which has the composition shown in Table 2 of geometric capacity 1400mAh which regulated cell capacity in the positive electrode were constituted. The positive-electrode charge collector to which a sign 8 connects an insulating gasket to among drawing 3, and a sign 9 connects a positive electrode 2 and the obturation board 7 electrically is shown.

[0041] The active material utilization factor of the nickel hydroxide which is a positive active material was examined according to the following conditions using these cells. Each test condition is shown below.

[0042] Positive-electrode capacity, i.e., the geometric capacity calculated from a nickel hydroxide active material, charged the bottom of each environment (0 degree C, 20 degrees C, and 45 degrees C) 150% by the charging current of 0.1CmA, the pause was performed for 3 hours, continuous discharge was performed to 0.1V to the mercury-oxide electrode by the low-current density of 0.2CmA(s) under 20-degree-C atmosphere, and the active material utilization factor was calculated using the following formula.

[0043] active material utilization factor = (the service capacity / nickel hydroxide geometric capacity x100 to 0.1V -- the result of these examinations is shown in drawing 4) Although the 20-degree C utilization factor of the cell using the positive electrode of No.P which is an example of comparison is as good as 97%, the utilization factor under 45-degree C atmosphere is 50%, and substantial service capacity falls. On the other hand, the 20-degree C utilization factor of the cell using the positive electrode of No.K-O

which is the example of this invention was 90 - 100%, and the utilization factor under 45-degree-C atmosphere is 70 - 85%, and showed the service capacity which was excellent in the broad temperature requirement. Thus, by adding the above-mentioned additive to a positive electrode shows that can raise the active material utilization factor under the elevated-temperature atmosphere of the nickel and the hydrogen battery which does not contain cadmium (45 degrees C), and the utilization factor which was excellent over the broad temperature requirement is shown. This is because the charge reaction to the oxy-nickel hydroxide of nickel hydroxide is fully performed in order for the added compound to stick to the front face of the nickel oxide which is an active material and to raise the overvoltage of the oxygen evolution which is the competitive reaction of the charge under elevated-temperature atmosphere.

[0044] Although the BET specific surface area measured by adsorption of nitrogen gas used the nickel hydroxide powder which is 22m²/g in this example, this BET specific surface area should just be set up within the limits of 10-30m²/g. This is because a substantial capacity will fall since tap density falls and the restoration nature of a positive electrode falls, if a reaction surface area will fall if it becomes below 10m²/g, an electric discharge property deteriorates and it becomes more than 30m²/g.

[0045] The lithium hydroxide in the electrolytic solution has desirable addition of 10 or more g/l in order to raise the utilization factor of nickel hydroxide, and discharge voltage.

[0046] Moreover, the zincic-acid ion which exists in the electrolytic solution can suppress expansion of the positive electrode by the repeat of electric discharge, and can raise reliability, such as a life property, further.

[0047] By this example, although surface density used 300g/the letter nickel porous body of foaming of m² for the base material, if surface density is within the limits of 200 - 700 g/m², the same effect is shown. Moreover, besides the letter nickel porous body of foaming, even if it uses the punching metal and plate which are a kind of a three-dimensions porous body, the same effect is acquired.

[0048] Furthermore, although this example explained what zinc and cobalt contained as the solid solution inside the crystal of nickel hydroxide, in addition to zinc and cobalt, that in which lead, silver, an indium, an yttrium, iron, and manganese exist as the solid solution in 1 - 7wt% can also be used, and these also show the same effect.

[0049] In addition, in this example, although an example of the nickel and the hydrogen battery of cylinder seal type was shown, the same effect is acquired also in square shape nickel and a hydrogen battery.

[0050]

[Effect of the Invention] As mentioned above, according to this invention, the nickel positive electrode which has the utilization factor which was excellent under elevated-temperature atmosphere by having added a kind at least among the compounds of an yttrium, an indium, antimony, barium, calcium, and beryllium all over the three-dimensions porous body which gives this conductivity for a principal component slack nickel oxide, or the nickel positive electrode which it is monotonous and comes to support is obtained. [0051] Moreover, the three-dimensions porous body or the nickel positive electrode which it is monotonous and comes to support which gives this conductivity for a principal component slack nickel oxide, In nickel and a hydrogen battery equipped with the negative electrode which makes a subject electrochemically the hydrogen storing metal alloy in which the occlusion release reaction of hydrogen is

possible, the alkali electrolytic solution, separator, the case where these are held, and the obturation board that has a relief valve The aforementioned nickel positive electrode at least among nickel hydroxide powder, and a cobalt oxide and a zincic-acid ghost A kind, By containing a kind at least among the compounds of an yttrium, an indium, antimony, barium, calcium, and beryllium The nickel and the hydrogen battery which has the utilization factor which was excellent over the broad temperature requirement are obtained without containing a heavy metal called cadmium.

[Translation done.]